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Kuchanov, S.I.; Kok, C; ten Brinke, G.

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Molecular Inhomogeneity and Scattering Properties of Products of "Living" Anionic Copolymerization

Semion Kuchanov*

Polymers & Crystals Chair, Physics Department,
Lomonosov Moscow State University, Vorobjevi Gori, 117234 Moscow, Russia

Christiaan Kok and Gerrit ten Brinke*

Department of Polymer Chemistry, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT: A quantitative theory of anionic copolymerization of an arbitrary number of monomers has been developed to calculate the rate of this process as well as the parameters characterizing the composition and chemical structure of the gradient macromolecules formed. Equations have been derived for the angular dependence of the amplitude of scattering of the melt of these copolymers as well as its spinodal. The theory elaborated for batch "living" anionic copolymerization has been extended to semibatch regimes where the reaction mixture is continuously fed by a solution of monomers. Equations have been derived providing the possibility to establish the dependence of the intramolecular inhomogeneity of the products of semibatch copolymerization on the monomer feed rate and composition. With the theoretical approach developed, it is possible to efficiently control the chemical structure of the copolymers at each stage of their synthesis which is of utmost importance for obtaining polymeric materials with desired properties.

1. Introduction

In the majority of theoretical papers dealing with linear copolymers, the authors restrict their consideration to intramolecularly homogeneous copolymers. If any macromolecule constituting a specimen of such a copolymer is cut arbitrarily into rather long fragments, their average composition and sequence distribution will be practically the same as those of the initial macromolecule. This property is characteristic for most copolymers synthesized by methods of free-radical copolymerization and copolycondensation.

Among copolymers showing intramolecular inhomogeneity, the most extensively studied theoretically and experimentally are block copolymers. Their synthesis is traditionally performed in several stages.[1−7] Thus, for instance, to obtain a diblock copolymer one of the monomers is first polymerized in the presence of an anionic initiator and the active homopolymer. Then it is put into the medium of the other monomer, the polymerization of which results in the formation of the second block. If both monomers are loaded simultaneously and "living" anionic polymerization is conducted in one stage, the copolymer prepared will in many cases have a gradient composition profile along the chain (see Figure 1c,d). Experimental verification of this fact has been repeatedly reported in the literature.[8−23]

Binary anionic copolymerization of styrene with diene monomer (butadiene or isoprene) in the presence of an initiator based on alkali metal is likely to be the most thoroughly investigated. For instance, in the organolithium-initiated copolymerization of isoprene and styrene in hydrocarbon solvents, isoprene is generally polymerized almost exclusively at the first stage of the process, followed by polymerization of styrene to give a terminal polystyrene block.[8−13] An analogous situation occurs when isoprene is replaced by butadiene.[14−23] The products formed for such a process at complete conversion of monomers are so-called *tapered* block copolymers (TBC).[13,14,23,24] These macromolecules differ from those of *ideal* block copolymers (IBC) by two features. First, the border between the blocks of the chains of TBC is more or less fuzzy, whereas for the chains of IBC it proves to be of a stepwise character. Second, the blocks of macromolecules of TBC can contain both monomers.

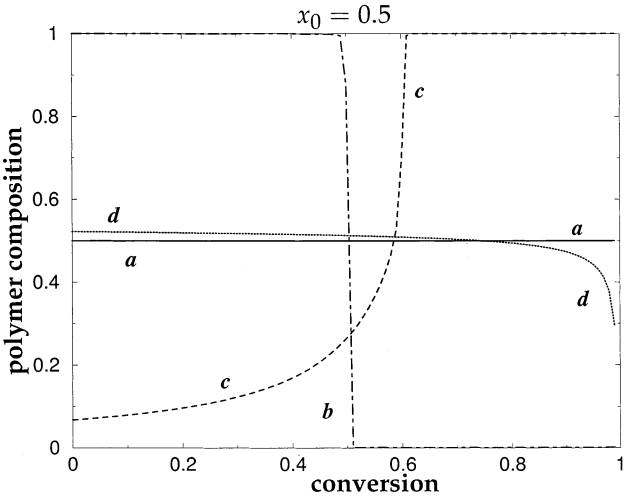

Figure 1. Examples of the shape of the polymer composition ($X_A(p)$) vs the conversion (p) for some binary systems: (a) homogeneous copolymer; (b) ideal block copolymer; (c) styrene/butadiene in toluene with lithium counterion ($r_1 = 0.004$, $r_2 = 12.9$);[25] (d) styrene/butadiene in toluene with sodium counterion ($r_1 = 0.42$, $r_2 = 0.30$).[26]

To ensure the formation of TBC in the course of "living" anionic copolymerization one of the values of the reactivity ratios r_1 and r_2 should be large and the other one small as compared to unity. In the limiting case of $r_1 \to 0$, $r_2 \to \infty$ we will have IBC, while with a decreasing difference in values of r_1 and r_2 the border

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between the blocks becomes more and more fuzzy until its width is comparable with the size of a macromolecule. Here the formation of gradient statistical copolymers (GSC) rather than TBC occurs as a result of the copolymerization process.

The indisputable advantage of anionic copolymerization over free-radical copolymerization is the possibility to control efficiently the reactivity ratios by varying the synthesis conditions. Thus, in the course of copolymerization of styrene with butadiene in toluene, the use of an organosodium initiator instead of an organolithium one leads under analogous conditions to a change in values of the reactivity ratios from $r_1 = 0.004$, $r_2 = 12.9$[25] to $r_1 = 0.42$, $r_2 = 0.30$,[26] whereas recourse to an organopotassium initiator yields the values $r_1 = 3.3$, $r_2 = 0.12$.[27] These examples convincingly show how a variation in counterion leads to a pronounced change in the kinetic parameters of anionic copolymerization in nonpolar hydrocarbon solvents. The reactivity ratios are influenced to no lesser extent by the presence in the reaction system of polar substances like ethers or amines.[13,14,17,19−23] So, the addition to benzene or cyclohexane of even a trace amount of tetrahydrofuran can be responsible for a dramatic change in the primary structure of the macromolecules formed. Namely, it results in a strong increase of the intramolecular mixing of different type monomer units along the copolymer chains, i.e., to an increase of their "taper" character.[13,17,21−24] Thus, varying the concentration of tetrahydrofuran or another analogous polar "randomizer" of copolymer chains, a directed synthesis of macromolecules with prescribed degree of intramolecular inhomogeneity can be carried out.

An experimental study of tapered block copolymers (TBC) and ideal block copolymers (IBC) (synthesized, respectively, by simultaneous and sequential anionic copolymerization) of identical composition, molecular weight, and polydispersity has revealed a number of substantial advantages of the former.[13,24] This concerns mechanical properties of block copolymers of styrene with isoprene[13] as well as blends of polystyrene with polyethylene to which poly(hydrogenated butadiene-*b*-styrene) copolymers have been added as emulgators.[24] When going from IBC to TBC a change in microdomain morphology, accompanied by a marked increase in the stabilizing power of the corresponding block copolymers, has been observed. Besides, it has been established[13] that the temperature, below which the examined specimens of poly(styrene-*b*-isoprene) undergo microphase separation, turns out to be 50 °C lower for TBC in comparison with IBC.

The influence of the intramolecular inhomogeneity of butadiene−styrene copolymers on their dynamic and reologic properties has been studied by Kraus et al.[21,22] They synthesized these copolymers using organolithium initiator in the presence of a randomizer varying its concentration. These authors thus managed to obtain a series of specimens with an intramolecular composition profile $P_1(i)$ intermediate between the two extreme cases a and b in Figure 1. It has been established that the intramolecular inhomogeneity can affect dramatically the position and width of the dynamic loss peaks,[21] as well as the melt viscosity.[22]

Rather impressive results on the morphology of the microphase-separated domain structure for TBC of styrene + isoprene[13,23] and styrene + butadiene[23] have been obtained by Hashimoto and co-workers by using electron microscopy and small-angle X-ray scattering. First, the image contrast of the two phases in TBC microstructures is markedly weaker than for the IBC, which is due to substantial mixing of the incompatible monomeric units $\bar{M}_1$ and $\bar{M}_2$ within each domain. Second, micrographs of some specimens exhibit moiré patterns, which have never been observed in the cylindrical or lamellar microdomain morphology of IBC systems. Such patterns seem to suggest a uniplanar arrangement of the lamellae of rods with misaligned orientation of their axes in the successive planes.

Despite the fact that TBCs have been first synthesized long ago, to the authors' knowledge, no approach providing a general quantitative description of these copolymers has been developed so far. The authors of the paper cited as ref 28 seem to be the first to devote special attention to *intramolecular* chemical inhomogeneity (IntraCI) of the products of "living" copolymerization. They proposed for it the term "chemical inhomogeneity of the second type" to distinguish it from the traditional *intermolecular* chemical inhomogeneity (InterCI). The Monte Carlo simulation method was employed for determining probabilities $P_1(i)$ to find a monomeric unit $\bar{M}_1$ at the ith position from the beginning of a growing polymer chain.[29] A similar problem has been addressed by means of computer simulation using the cooperative motion algorithm,[30] the application of which allowed one to predict thermodynamic as well as other properties of gradient copolymers. Particularly, the dependence of the static collective structure factor on the wave vector was explored for a number of systems representing copolymers with various distributions of monomeric units along the chains.

Our paper deals with the solution of some fundamental problems of the anionic copolymerization theory. The first set concerns the quantitative dependencies of the parameters characterizing the chemical structure of the copolymers on the conditions of their synthesis, i.e., on the stoichiometric and kinetic parameters as well as on the injection of monomers into the reaction zone. Among the problems of the second set is that of establishing correlations between the conditions of the synthesis of gradient copolymers and their scattering as well as thermodynamic properties.

The present paper deals with kinetically controlled anionic copolymerization under conditions where depolymerization reactions may be ignored. In contrast to this, copolymerization by a "living" polymer mechanism[31] corresponds to the situation where the rates of propagation and depropagation reaction of a polymer chain are the same. In such systems polymer chains and monomers are at every moment in thermodynamic equilibrium. Shifting it by a temperature- or pressure variation allows one to conduct an equilibrium copolymerization. There are several publications (see, for instance, refs 32−39) devoted to its quantitative theory, some of which[38,39] invoke a rather sophisticated mathematical apparatus. Unlike such "living" copolymerizations, where the chain growth is thermodynamically controlled, the model of "living" copolymerization considered by us is almost unexplored theoretically. Our major objective is therefore to make up for this deficiency.

The paper is organized as follows. The next section is devoted to the elaboration of the theoretical approach for the calculation of the dependence of the overall conversion of monomers on time, to the solution of the

sequence distribution problem and to the quantitative assessment of the degree of intramolecular inhomogeneity of GSC. In the subsequent section an algorithm is formulated enabling one to find any statistical characteristics of the chemical structure of "living" anionic copolymerization products. This algorithm is employed to derive equations for chemical correlators that are indispensable for constructing phase diagrams of melts and solutions of copolymers. Expressions for the structure factor are reported in the fourth section within the framework of the assumption of an incompressible system. In the fifth section the theory is extended to semibatch copolymerization where the effect of the rate and composition with which a reaction system is fed by a solution of monomers on the composition and chemical structure of the GSC macromolecules formed is investigated. The efficiency of the general approach advanced in this work is exemplified by numerical calculations of real and hypothetical systems with fixed sets of kinetic parameters.

2. Quantitative Theory of "Living" Copolymerization

Let us consider homogeneous copolymerization of an arbitrary number m of monomers conducted by the anionic mechanism. In deciding on a particular kinetic model we will proceed from the commonly accepted assumptions.[1−7]

(1) Chain transfer and chain termination reactions are absent.

(2) The constant $k_{\alpha\beta}$ of the rate of the addition of monomer M_β to a macroion R_α with αth type terminal unit does not depend on the degree of polymerization l of this macroion for any α and β (the Flory principle).

(3) The duration of the initiation stage, in which the concentration of growing chains attains a stationary value R^0, was found to be far less than the propagation time. This condition enables one to think of initiation as an instantaneous process and thus to assume that all polymer chains start to grow simultaneously.

Within the framework of such simplest kinetic model the set of material balance equations, describing the change with time t of the concentrations $R_\alpha(l)$ of growing chains of length l and α-type terminal unit, is

$$\frac{dR_\alpha(l)}{dt} = M_\alpha \sum_{\beta=1}^{m} k_{\beta\alpha} R_\beta(l-1) - R_\alpha(l) \sum_{\beta=1}^{m} k_{\alpha\beta} M_\beta \quad (1)$$

To obtain a closed set of equations, this should be supplemented with the equations for the monomer concentrations M_α

$$\frac{dM_\alpha}{dt} = -\sum_{\beta=1}^{m} k_{\beta\alpha} R_\beta M_\alpha, \quad \text{where } R_\alpha \equiv \sum_{l=1}^{\infty} R_\alpha(l) \quad (2)$$

The fraction ρ_α of αth type active centers (ions) among all those involved in the system can be determined by the expression

$$\rho_\alpha \equiv \frac{R_\alpha}{R^0} = \frac{x_\alpha B_\alpha}{k_{\alpha\alpha} w(\boldsymbol{x})}, \quad \text{where } w(\boldsymbol{x}) \equiv \sum_{\beta=1}^{m} \frac{x_\beta B_\beta}{k_{\beta\beta}} \quad (3)$$

where the numerator is a uniform polynomial of degree $(m-1)$ with respect to the components $x_1, ..., x_\alpha, ..., x_m$ of the vector $\boldsymbol{x}$, each of which, $x_\alpha = M_\alpha/M (\alpha = 1, ..., m)$, is equal to the molar fraction of free monomers M_α in the reaction system. Here M is the molar concentration of all free monomers. The polynomials $x_\alpha B_\alpha(\boldsymbol{x})$, whose coefficients depend solely on the reactivity ratios $r_{\alpha\beta} \equiv k_{\alpha\alpha}/k_{\alpha\beta}$ ($\alpha,\beta = 1, ..., m$), can be found from the solution of a set of linear equations for R_α, obtainable by the summation over l of all terms of eq 1. The differential equations for R_α are by virtue of the Bodenstain principle reducible to algebraic equations coinciding with those which describe the fractions ρ_α of active centers in the processes of free-radical copolymerization. A simple graph-theoretic algorithm has been put forward[40,41] making it possible to write down the polynomials $x_\alpha B_\alpha$ in a form convenient for the calculation of their values at any given composition of the monomer mixture x. The evolution of the latter with molar conversion $p = 1 - M/M^0$ is described by the solution of the set of equations

$$(1-p)\frac{dx_\alpha}{dp} = x_\alpha - X_\alpha(\boldsymbol{x}), \quad x_\alpha(0) = x_\alpha^0 (\alpha = 1,..., m) \quad (4)$$

where the following designations are used:

$$X_\alpha = \frac{\Pi_\alpha}{\Pi}, \quad \Pi = \sum_{\alpha=1}^{m} \Pi_\alpha, \quad \Pi_\alpha = x_\alpha B_\alpha \hat{\sigma}_\alpha,$$

$$\hat{\sigma}_\alpha = \sum_{\beta=1}^{m} r_{\alpha\beta}^{-1} x_\beta \quad (5)$$

Equation 4, which can be easily derived from eq 2 with allowance for eqs 1 and 3, are familiar from the theory of free-radical copolymerization.[41,42] There $\boldsymbol{X}$ represents the instantaneous composition of a copolymer formed at a given monomer mixture composition $\boldsymbol{x}$. However, for the process of "living" copolymerization of interest the vector $\boldsymbol{X}$ has a quite different meaning, which will be explained below in more detail.

To describe the kinetics of "living" anionic copolymerization it is necessary to write down the equation for the rate of change of conversion p with time t

$$\frac{dp}{dt} = (1-p) R^0 \sum_{\alpha}\sum_{\beta} k_{\alpha\beta}\rho_\alpha x_\beta = (1-p) R^0 \frac{\Pi(\boldsymbol{x})}{w(\boldsymbol{x})} \quad (6)$$

which is obtained by summation both sides of eq 2 over α. The integration of eq 6 along with eqs 3−5 allows one to find the kinetic curve $p(t)$ of the process under consideration.

The evolution with time of the distribution $\rho_\alpha^l \equiv R_\alpha(l)/R^0$ of growing polymer chains with αth type terminal unit can be obtained from the solution of the set of kinetic equations in eq 1 and can be conveniently rewritten in the integral form

$$\rho_\beta^l(t) = \int_0^t d\eta \sum_\gamma \rho^{l-1}(\eta) k_{\gamma\beta} M_\beta(\eta) \exp\{-\int_\eta^t \sigma_\beta(\xi) d\xi\} \quad (l \geq 2)$$

$$\rho_\beta^1(t) = \nu_\beta \exp\{-\int_0^t \sigma_\beta(\xi) d\xi\}, \quad \text{where } \sigma_\alpha \equiv \sum_\beta k_{\alpha\beta} M_\beta = k_{\alpha\alpha} M \hat{\sigma}_\alpha \quad (7)$$

where ν_β is the initial fraction of type β active centers. It can be readily shown that in the limit of $l \to \infty$ the

distribution $\rho_\alpha^l(t)/\rho_\alpha(t)$ can be described by the Poisson formula, the only parameter of which is $l_m p$. The latter represents the average length $\bar{l}$ of the growing chains and increases with conversion p from 0 up to its maximum value l_m given by $l_m = M^0/R^0$. For $\bar{l} \gg 1$, the Poisson distribution is known[32] to be very narrow, being more narrow the greater $\bar{l}$ is. This property underlies the theoretical consideration of copolymers of practical importance as being monodisperse in length. This important conclusion is identical to that which Flory made many years ago[44] when dealing with "living" homopolymerization.

In the case of interest of copolymerization at $\bar{l} \gg 1$, the polydispersity of the macroions formed may in a first approximation be neglected not only with respect to the chemical size l but also with respect to the chemical composition. Such an assertion is quite evident, bearing in mind that the products of "living" copolymerization are composed of chains of the same length l, which have grown under perfectly identical conditions.

In the absence of strongly pronounced InterCI, the copolymers synthesized up to high conversions by an anionic mechanism may exhibit substantial IntraCI. In the simplest way it is possible to characterize this by means of the vector-function $\boldsymbol{P}(i)$ whose components $P_\alpha(i)$ ($\alpha = 1, ..., m$) represent the probability for a monomeric unit located i units from the beginning of a randomly chosen chain to be of type α. As for $P_0(i)$, it is equal to the probability for a randomly chosen chain to comprise less than i units. In the absence of polydispersity in length of the macroions we have $P_0(i) = 0$ for all $i < l$ and the vector $\boldsymbol{P}(i)$ upon the exclusion of its zeroth component may be thought of as an m-component one. First we discuss the fundamental distinctions in behavior of the vector-function $\boldsymbol{P}(i)$ for copolymer chains synthesized by free-radical and ionic mechanisms.

For the products of radical copolymerization prepared at any fixed conversion the vector $\boldsymbol{P}(i)$ rapidly tends with increasing i to the vector $\boldsymbol{X}$ of the instantaneous copolymer composition. Already at values $i \sim 10$, the difference between $\boldsymbol{P}$ and $\boldsymbol{X}$ proves to be, as a rule, almost indistinguishable.[45] This initial portion of the macromolecule may well be neglected in view of its minuteness as compared to the whole chain, which allows us to consider $\boldsymbol{P}(i) = \boldsymbol{X}$ over its entire length. To find the average composition of a copolymer $\langle \mathbf{X} \rangle$, present in the reaction mixture at conversion p, it is necessary to average its instantaneous value $\boldsymbol{X}$ over all conversions p' preceding p

$$\langle X_\alpha \rangle \equiv \frac{1}{p}\int_0^p X_\alpha \, \mathrm{d}p' = \frac{x_\alpha^0 - (1-p)x_\alpha}{p} \quad (\alpha = 1,..., m) \tag{8}$$

where the dependence of the monomer mixture composition $\boldsymbol{x}$ on the conversion p is obtainable from the solution of eq 4.

In the processes of "living" copolymerization $P_\alpha(i)$ resembles curve *a* in Figure 1 only when the process is conducted under an initial composition x^0 close to the azeotropic one. In other cases these probabilities exhibit a clear dependence on i.[29] Within the framework of the approach discussed, it can be rigorously shown that the value of the probability $P_\alpha(i)$ for the products of anionic copolymerization exactly coincides with the component X_α of the vector of instantaneous composition of a copolymer formed by the free-radical mechanism, provided the value of conversion is $p = i/l_m$. By way of illustration Figure 1*c* presents the theoretical dependence $P_1(i)$ for copolymers of styrene and butadiene prepared by the anionic polymerization technique at values of reactivity ratios $r_1 = 0.004$, $r_2 = 12.9$ found earlier[25] for this system. Because of the dramatic difference in the values of r_1 and r_2 two domains can be observed, separated by a rather sharp boundary. The first region corresponds to a statistical copolymer of butadiene and styrene with small fraction of the latter, whereas the second one corresponds to almost pure styrene homopolymer. With increasing difference between the reactivity ratios, TBC will bear closer resemblance to IBC. Conversely, as this difference decreases, the boundary between the two blocks will become more and more fuzzy while these blocks will degenerate as the fractions of incorporated and original units become comparable. In the latter case, instead of TBC we will have merely gradual copolymers with smoothly changing dependence $P_\alpha(i)$ (curve *d* in Figure 1), which can be obtained by varying the synthesis conditions (temperature, solvent, catalyst). The theoretical results reported in this paper can be applied for the description of such copolymers as well.

To compare quantitatively the degree of intramolecular inhomogeneity of binary anionic copolymers, it is convenient to introduce the parameter

$$\delta \equiv \frac{1}{l}\int_0^l [P_\alpha(i) - \overline{\zeta_\alpha}]^2 \, \mathrm{d}i \tag{9}$$

Its value coincides with that of the dispersion of the composition distribution of the free-radical copolymerization products

$$\sigma^2 \equiv \frac{1}{p}\int_0^p [X_\alpha(p') - \langle X_\alpha \rangle]^2 \, \mathrm{d}p' \tag{10}$$

at the values of reactivity ratios r_1, r_2 and conversion identical to those of the anionic process. For the copolymers with distributions $P_1(i)$ presented in Figure 1, the parameter δ equals, respectively, 0 (a), $^1/_4$ (b), 0.17 (c), and 0.008 (d). Clearly, for increasing intramolecular inhomogeneity the parameter δ increases reaching its maximum possible value $\delta = {}^1/_4$ in the case of IBC.

In terms of the approximation discussed the solution of the problem of composition and sequence distribution of the products of "living" copolymerization can be reduced to that already solved earlier in the theory of free-radical copolymerization. Thus, the fraction of units $\bar{M}_\alpha$ in a copolymer synthesized by anionic mechanism can be calculated using expression 8, while for dyad fractions the following expressions hold:[41,42,47]

$$\frac{1}{l}\int_0^l P_\alpha(i)\, \nu_{\alpha\beta}(i) \, \mathrm{d}i = \frac{1}{p}\int_0^p X_\alpha(\boldsymbol{x}(p'))\nu_{\alpha\beta}(\mathrm{x}(p')) \, \mathrm{d}p' = \langle P(\bar{M}_\alpha \bar{M}_\beta) \rangle \tag{11}$$

Here $\nu_{\alpha\beta}(\boldsymbol{x})$ denotes the elements of the transition probability matrix of the Markov chain describing the instantaneous sequence distribution of monomeric units in macromolecules obtained in the course of free-radical copolymerization at monomer feed composition $\boldsymbol{x}$. Relationships 11 are a particular case of more general ones, according to which the probability of any sequence containing several units in the products of both "living" and free-radical copolymerization is the same at any identical values of reactivity ratios and conversion. This

circumstance allows one, when solving the problem of sequence distribution in copolymers prepared by the anionic copolymerization technique, to take advantage of an already devised software modeling tool[48] that provides the possibility to calculate the change with conversion of the quantities X_α (eq 5), $\langle X_\alpha \rangle$ (eq 8), and the probabilities of the sequences up to four units for the processes of free-radical multicomponent copolymerization.

3. Chemical Correlators

A obvious question to be answered when developing the theory of anionic copolymerization is whether the knowledge of the distribution $\boldsymbol{P}(i)$ suffices to provide an exhaustive description of the intramolecular inhomogeneity of the products obtained. For such a description, in line with the general principles of statistical chemistry of polymers,[42] it is indispensable to know the probability measure on the set of all realizations of a stochastic process of conventional movement along the polymer chain. At every step of such a movement a jump occurs whose length is equal to one monomeric unit. An αth type unit may either go over into a βth type unit or leave the macromolecule. The first option corresponds to a transition from the αth regular state to the βth regular state ($\alpha,\beta = 1, ..., m$), while the second option corresponds to a transition to the absorbing state to which the index $\beta = 0$ is assigned. Once attained, it is impossible, by definition, to abandon this state. A stochastic process of this kind with discrete time and a discrete set comprising $(m + 1)$ states is referred to in mathematics as a stochastic chain.[49] The best known among these is the Markov chain, for which the probability of reaching the βth state is controlled exclusively by the type α of the last state, irrespective of all the preceding ones. If this probability $\nu_{\alpha\beta}$ is time independent such a Markov chain is termed homogeneous. It is uniquely characterized by the matrix of transition probabilities with elements $\nu_{\alpha\beta}$ and the vector $\boldsymbol{\nu}$, whose components $\nu_\alpha(\alpha = 1, ..., m)$ are equal to the probabilities of the initial states.

The mathematical apparatus of the theory of homogeneous Markov chains is extensively applied for the quantitative description of the sequence distribution and composition inhomogeneity of the products of free-radical copolymerization.[42,47,50] When the synthesis is performed by this method the time of macroradical growth is markedly less than the duration of the synthesis process, and consequently, during the period of the formation of a macromolecule the monomer mixture composition in the reaction system has no time to change. In view of this circumstance, the transition probabilities $\nu_{\alpha\beta}$ of the Markov chain, describing the chemical structure of macromolecules formed at any fixed monomer conversion, may be regarded as being constant. However, for the statistical characteristics of the chemical structure of the products of anionic copolymerization the homogeneous Markov chain does not work, because of an appreciable change in monomer mixture composition. As a consequence intramolecular chemical inhomogeneities, absent in the products of radical polymerization, are known to appear in the polymer chains.

To establish the type of the stochastic process of conventional movement along a macromolecule describing anionic copolymers, we will distinguish monomeric units not only by type α but also by the moments τ of formation due to monomer addition to the growing chain. The infinitesimal probability $dP^i_\alpha(t;\tau)$ to find at moment t at position i of a polymer chain an αth type unit being formed within the interval from τ up to $\tau + d\tau$ is determined by the expression

$$dP^i_\alpha(\tau;t) = \Theta^i_\alpha(\tau)\eta_s(t - \tau)\, d\tau$$
$$\Theta^i_\alpha(\tau) = \sum_\beta \rho^{i-1}_\beta(\tau) k_{\beta\alpha} M_\alpha(\tau) \ (i \geq 2), \quad \Theta^1_\alpha(\tau) = \nu_\alpha \delta(\tau) \tag{12}$$

where $\eta_s(t - \tau)$ stands for the step-function equal to 1 at $\tau < t$ and to 0 at $\tau > t$. The label τ, which we use to mark monomeric units, is introduced for convenience; only the distribution of unlabeled units

$$P^i_\alpha(t) = \int_0^t \Theta^i_\alpha(\tau)\, d\tau \quad (i \geq 2), \quad P^1_\alpha(t) = \nu_\alpha \tag{13}$$

has a physical meaning. The functions $\Theta^i_\alpha(\tau)$ ($\alpha = 1, ..., m$), which can be considered as components of the vector $\Theta^i(\tau)$, are the probability densities to find at the ith position of a polymer chain a unit of a particular type α with label τ. These functions satisfy the recurrence relationship

$$\Theta^{i+1}_\alpha(\tau) = \int_0^\tau d\eta \sum_\beta \Theta^i_\beta(\eta) K_{\beta\alpha}(\eta,\tau) \quad (i \geq 2) \tag{14}$$

where the following designation is used

$$K_{\beta\alpha}(\eta,\tau) \equiv \exp\{-\int_\eta^\tau \sigma_\beta(\xi)\, d\xi\} k_{\beta\alpha} M_\alpha(\tau) \tag{15}$$

This relationship can be obtained immediately from (7) and (12), provided the designations in the former are changed as $l \rightarrow i$ and $t \rightarrow \tau$ and both its parts are summed over the subscript β after having been multiplied by the factor $k_{\beta\alpha}M_\alpha(\tau)$.

It can be readily noted that relationship 14 admits a simple probabilistic interpretation in terms of stochastic processes inasmuch as it describes the Markovian process of conventional movement along a macromolecule with labeled units. Each state of this process may be characterized by a pair of quantities (α,τ), the first of which is discrete whereas the second one is continuous. The probability density of reaching such a state at the $(i + 1)$th step depends, according to expression 14, only on the state at the preceding ith step. This argues for the Markovian character of the stochastic process describing anionic copolymers with labeled units. The matrix $\boldsymbol{K}(\eta,\tau)$ with the elements (15) plays for this stochastic process a role identical to that of the transition matrix for the Markov chain. Thus, expression $K_{\beta\alpha}(\eta,\tau)\, d\tau$ at $\alpha \neq 0$ corresponds to the infinitesimal probability to attain from labeled unit (β,η) by a single step along a macromolecule an αth type unit formed within the interval from τ to $\tau + d\tau$. Integrating $K_{\beta\alpha}(\eta,\tau)$ over τ from η up to t and summing over α from 1 up to m, we will get the probability for the unit (β,η) not to be located at the end of a macromolecule at the moment t

$$\int_\eta^t \sum_{\alpha=1}^m K_{\beta\alpha}(\eta,\tau)\, d\tau = 1 - T_{\beta 0}(\eta, t),$$
$$T_{\beta 0}(\eta, t) \equiv \exp\{-\int_\eta^t \sigma_\beta(\xi)\, d\xi\} \tag{16}$$

The probability $T_{\beta 0}(\eta, t)$ of the transition from the state (β,η) to the absorbing state coincides with the probability for βth type unit formed at moment η to remain the terminal one until moment t. Using relationship 16 it can be verified, proceding from expression 14, that the probability densities $\Theta^i_\beta(\tau)$ satisfy the normalization condition.

The vector $\Theta^i(\tau)$ components, determining in accordance with (13) the distribution $\boldsymbol{P}^i(t)$, can be found in line with (14) as a result of the effect upon Θ^1 of the operator $K^{(i-1)}$. This represents the $(i-1)$th degree of the matrix-integral operator K with kernel (eq 15).

As emphasized in the foregoing, under the condition $\bar{l} = l_m p \gg 1$, the variable i may be thought of as continuous, and it is thus possible to approximate the distribution ρ^i_β by a monodisperse one $\rho_\beta(p')\delta(i - l_m p')$. Within the framework of this approximation the recourse to formulas 12, 13, and 6 results in the following simple expression

$$P^i_\alpha(t) \equiv P_\alpha(i) = X_\alpha(i/l_m)\eta_s(l_m p - i) \tag{17}$$

where p represents the conversion of monomers at moment t, whereas the dependence $X_\alpha(p)$ is known from the theory of free-radical copolymerization according to eqs 4 and 5.

The description of the chemical structure of the copolymers may be accomplished at least in two ways. The first one is carried out by setting the probabilities of sequences U_k containing $k = 2, 3, ...,$ monomeric units. As distinct from this traditional way, sometimes it appears more convenient to describe the sequence distribution in linear copolymers in terms of *chemical correlators*.[42,51] The simplest among them, $Y_{\alpha\beta}(k)$, corresponds to the joint probability to find two randomly chosen monomeric units M_α and M_β on a macromolecule separated by an arbitrary sequence U_k. This correlator plays an important role in the thermodynamics of solutions and blends of heteropolymers since its *generating function* (gf)

$$W_{\alpha\beta}(x) \equiv \sum_{k=0}^{\infty} Y_{\alpha\beta}(k)x^{k+1} \tag{18}$$

enters into the expression for the spinodal.[52] As will be shown in section 4, the knowledge of $W_{\alpha\beta}(x)$ enables one to find the angular dependence of the scattering amplitude, i.e., the static scattering function. It is possible to define the three-point chemical correlator $Y_{\alpha\beta\gamma}(k_1,k_2)$ as the joint probability to find three randomly chosen units M_α, M_β, and M_γ separated by arbitrary sequences comprising k_1 and k_2 units. The gf of this correlator $W_{\alpha\beta\gamma}(x_1,x_2)$ enters into the equations for the critical points of the phase diagram of solutions and blends of heteropolymers.[52] In a similar manner it is possible to define the n-point chemical correlators, the knowledge of the gf of which is critical for deriving expressions for the coefficients of the expansion of the Landau free energy.[52] All these gf's can be found in a standard way provided the expression for *generating functional of chemical correlators* (GFCC) is known. For example the gf of the two-point correlator (eq 18) is expressed through the second-order variational derivative of GFCC $\hat{\mathcal{G}}[\{\boldsymbol{s}^i\}]$

$$W_{\alpha\beta}(x) = \frac{1}{l}\sum_{i=1}^{\infty}\sum_{j=i+1}^{\infty} x^{j-i}\int_0^t d\tau \int_0^\tau d\eta \left.\frac{\delta^2\hat{\mathcal{G}}[\{\boldsymbol{s}^i\}]}{\delta s^i_\alpha(\eta)\delta s^j_\beta(\tau)}\right|_{\{\mathbf{s}^i\}=1} \tag{19}$$

Similarly, the gf of chemical correlator of any order is expressible through the variational derivative of the same order of GFCC, taken at vector-functions $\boldsymbol{s}^1(\tau_1)$, $\boldsymbol{s}^2(\tau_2)$, ..., all components of which are equal to unity.

The GFCC of a stochastic Markovian process of conventional movement along chains of labeled units, describing the products of anionic copolymerization, has the following form

$$\hat{\mathcal{G}}[\{\boldsymbol{s}^i\}] = \sum_{n=1}^{\infty}\sum_{\{\alpha_i\}}\int\cdots\int_{\tau_1<\tau_2<\cdots\tau_{n-1}<\tau_n} \nu_{\alpha_1} s^1_{\alpha_1}(\tau_1)\delta(\tau_1) \prod_{i=2}^{n} K_{\alpha_{i-1}\alpha_i}(\tau_{i-1},\tau_i)s^i_{\alpha_i}(\tau_i)\, d\tau_i\, T_{\alpha_n 0}(\tau_n, t) \tag{20}$$

Substituting the functional eq 20 into formula 19 leads to the following expression for the gf of the two-point correlators

$$W_{\alpha\beta}(x) = \frac{1}{l}\int_0^t d\tau \int_0^\tau d\eta \Theta_\alpha(\eta)L_{\alpha\beta}(x;\eta,\tau) \tag{21}$$

where the following designation is used

$$\Theta_\alpha(\eta) \equiv \sum_{i=1}^{\infty}\Theta^i_\alpha(\eta) = \nu_\alpha\delta(\eta) + \sum_\beta \rho_\beta(\eta)k_{\beta\alpha}M_\alpha(\eta) \tag{22}$$

while the elements $L_{\alpha\beta}$ of the matrix $\boldsymbol{L}$ can be found from the solution of the following set of integral equations

$$L_{\alpha\beta}(x;\eta,\tau) = xK_{\alpha\beta}(\eta,\tau) + x\int_\eta^\tau \sum_\gamma K_{\alpha\gamma}(\eta,\xi)L_{\gamma\beta}(x;\xi,\tau)\, d\xi \tag{23}$$

Given the vector-function $\Theta(\eta)$ and the matrix-function $\boldsymbol{L}(x;\eta,\tau)$ the gf of the three-point correlator can be found

$$W_{\alpha\beta\gamma}(x_1, x_2) = \frac{1}{l}\int_0^t d\tau \int_0^\tau d\eta \int_0^\eta d\xi\, \Theta_\alpha(\xi)L_{\alpha\beta}(x_1;\xi,\eta)L_{\beta\gamma}(x_2;\eta,\tau) \tag{24}$$

as well as any other, the algorithm of the construction of which is evident.

These equations for finding the gf of chemical correlators of copolymers synthesized by anionic mechanism are exact within the framework of the kinetic model chosen. Of major interest for the application of the gf (eq 21) for the calculation of the scattering intensity of solutions and blends of these polymers are the values of the argument x close to unity. For such values of x, i.e., at $0 < Q = -\ln x << 1$, in the case $\bar{l} = l_m p \gg 1$, eq 23 has the following approximate solution

$$L_{\alpha\beta}(x;\eta,\tau) = \exp\{-y[p(\tau) - p(\eta)]\}\Theta_\beta(\eta), \quad \text{where } y = Ql_m \tag{25}$$

As for the components (eq 22) of the vector $\Theta(\eta)$, they satisfy under this approximation

$$\Theta_\alpha(\eta) = l_m X_\alpha(p(\eta))\frac{dp}{d\eta} \tag{26}$$

Equation 6 allows one to switch conveniently from integration over time to that over conversion. This leads to the following simple approximate expression for the gf (eq 21)

$$W_{\alpha\beta}(x) = \frac{l_m}{p}\int_0^p \mathrm{d}p \int_0^{p'} \mathrm{d}p'' \, X_\alpha(p'')X_\beta(p') \exp[-y(p' - p'')] \quad (27)$$

The extension of this expression to gf's of multipoint correlators is quite apparent.

4. Static Scattering Function

The scattering intensity I with wavelength λ at any angle θ with respect to the incident radiation can be calculated by expression[53]

$$I(q) = \sum_\alpha \sum_\beta a_\alpha a_\beta \tilde{S}_{\alpha\beta}(q), \quad \text{where } q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \quad (28)$$

where a_α is the scattering length of an αth type monomeric units. In view of the spatial isotropy of the system the Fourier components $\tilde{S}_{\alpha\beta}(q)$ of the elements $S_{\alpha\beta}(\boldsymbol{r})$ of the correlation matrix, and consequently, the scattering intensity will be dependent only on the modulus q of the wave vector $\boldsymbol{q}$. For incompressible systems, expression (28) can be written in the following manner

$$I(q) = -\sum_{\alpha<\beta} (a_\alpha - a_\beta)^2 \tilde{S}_{\alpha\beta}(q) \quad (29)$$

where the structural matrix $\tilde{S}(q)$ may be presented as[54]

$$\tilde{S}(q) = \rho[\mathbf{b} - \mathbf{b}(\tilde{\mathbf{X}} + \mathbf{b})^{-1}\mathbf{b}] \quad (30)$$

Apart from the overall density of monomeric units ρ two matrices enter into the right-hand side of this expression. One of them, **b**, describes the pair interactions of monomeric units. Its elements are in a simple manner connected with the elements of matrix **d** which is the inverse of the matrix χ of Flory−Huggins parameters

$$b_{\alpha\beta} = d_{\alpha\beta} - \sum_\beta d_{\alpha\beta} \sum_\alpha d_{\alpha\beta} \Big(\sum_\alpha \sum_\beta d_{\alpha\beta}\Big)^{-1} \quad (31)$$

The second matrix, $\tilde{\mathbf{X}}$, up to a factor ρ equal to the structure matrix $[\tilde{\kappa}](q)$, is expressed in terms of the generating functions of the two-point chemical correlators $W_{\alpha\beta}(x)$

$$\tilde{X}_{\alpha\beta}(q) \equiv \tilde{\kappa}_{\alpha\beta}(q)/\rho = X_\alpha\delta_{\alpha\beta} + W_{\alpha\beta}(x) + W_{\beta\alpha}(x), \quad x = e^{-Q} \quad Q = a^2q^2/6 \quad (32)$$

where a represents the size of a monomeric unit. Thus, equations 28−32 jointly with expression 21 provide an exact solution for the scattering function of a melt of copolymers obtained by "living" anionic copolymerization of an arbitrary number of monomer types.

The amplitude of scattering (eq 28) becomes infinite at the spinodal, where the spatially homogeneous state of a polymer liquid becomes absolutely unstable with respect to composition fluctuations. Such a stability loss may happen either at zero wave vector or at $q = q^* \neq 0$. These two cases will be referred to as the trivial and nontrivial spinodal branches, respectively. As for the trivial branch, it is determined, according to expressions

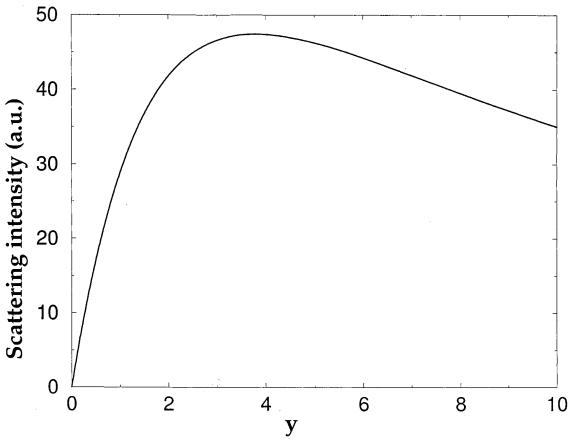

Figure 2. Shape of the scattering function as a function of the rescaled inverse length ($y = l_m a^2 q^2/6$) for an ideal block copolymer with an average composition of 0.5.

29 and 30, by the condition of vanishing of the determinant $D(q^2)$ of the matrix $\tilde{\mathbf{X}}(q) + \mathbf{b}$ at $q = 0$

$$D(0) = 0 \quad (33)$$

To find the nontrivial branch of the spinodal, where the null $q = q^*$ of the function $D(q^2)$ is doubly degenerate, it is necessary to solve a set of two equations

$$D(q^2) = 0 \quad \frac{\mathrm{d}D(q^2)}{\mathrm{d}q^2} = 0 \quad (34)$$

The solution of these equations results in an equation for the nontrivial spinodal hypersurface within the space of external parameters of the system in hand. At the Lifshitz points,[52] that are, by definition, the common points for the trivial and nontrivial branches of the spinodal, the value of q^* equals zero.

Within the framework of the approximation considered in section 2, the formulas for the calculation of the amplitude of scattering and the spinodal are substantially simplified because expression 32 is reducible in this case to the following form

$$\tilde{X}_{\alpha\beta}(q) = \frac{l_\mathrm{m}}{p}\int_0^p \mathrm{d}p' \int_0^p \mathrm{d}p'' \; X_\alpha(p')X_\beta(p'') \exp\{-y|\,p' - p''|\}, \quad y = Ql_\mathrm{m} = q^2\overline{R_\mathrm{G}{}^2}, \quad \text{where } R_\mathrm{G}{}^2 = a^2 l_\mathrm{m}/6 \quad (35)$$

Figures 2−4 present characteristic scattering curves for the different systems introduced in Figure 1. Figures 3 and 4 have been calculated in the long chain approximation using expression 35. Figure 3 corresponds to styrene/butadiene in toluene with lithium counterion. The resulting composition profile (curve c in Figure 1) resembles that of a diblock copolymer. The scattering curve for the case of an average composition of $x_1 = 0.5$ is very similar, both in shape and magnitude, to the scattering curve of the symmetric ideal block copoymer presented in Figure 2. For the case of the sodium counterion, where the reactivity ratios are similar, the scattering intensity is strongly reduced as demonstrated in Figure 4. In particular, for $x_1 = 0.5$, corresponding to curve d in Figure 1, the amount of scattering is as expected very small with only a very shallow maximum.

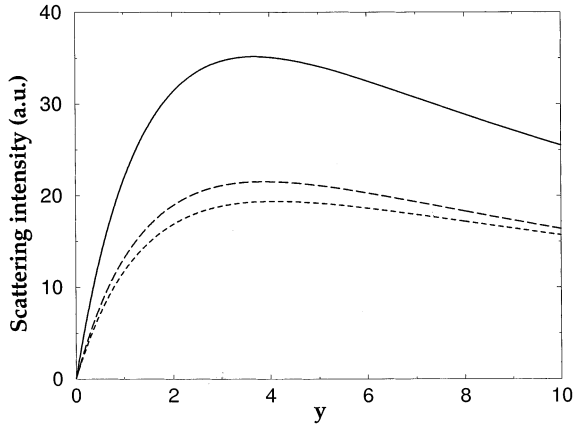

Figure 3. Scattering curve as a function of the rescaled inverse length ($y = l_m a^2 q^2/6$) for the products of anionic copolymerization of styrene and butadiene in toluene with lithium counterion ($r_1 = 0.004$, $r_2 = 12.7$)[25] for several average compositions. Key: (—) $x_1 = 0.25$; (— —) $x_1 = 0.5$; (- -) $x_1 = 0.75$.

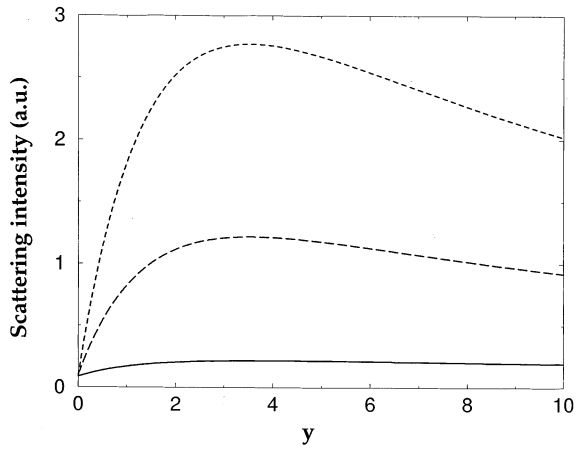

Figure 4. Scattering as a function of the rescaled inverse length ($y = l_m a^2 q^2/6$) for the products of anionic copolymerization of styrene and butadiene in toluene with sodium counterion ($r_1 = 0.42$, $r_2 = 0.30$)[26] for several average compositions. Key: (—) $x_1 = 0.25$; (— —) $x_1 = 0.5$; (- -) $x_1 = 0.75$.

When the spinodal is calculated, it is convenient to introduce the variables

$$z_\alpha(p';p) \equiv X_\alpha(p') - \langle X_\alpha \rangle \tag{36}$$

describing the difference between the conditional probability $P_\alpha(i)$ to find a unit $\bar{M}_\alpha$, located at $i = l_m p'$ distance from the beginning of the chain, and the unconditional probability $\langle X_\alpha \rangle$ (eq 8) to find such a unit at any place of a macromolecule. Function 36 determines the following integrals

$$I^{(0)}(y) \equiv \langle u^{(0)} \rangle, \quad I^{(1)}_\alpha(y) \equiv \langle u^{(1)}_\alpha \rangle, \quad I^{(2)}_{\alpha\beta}(y) \equiv \langle u^{(2)}_{\alpha\beta} \rangle \tag{37}$$

where the angular brackets denote the effect on the functions involved

$$u^{(0)} = 1, \quad u^{(1)}_\alpha = z_\alpha(p';p), \qquad u^{(2)}_{\alpha\beta}(p', p'';p) = z_\alpha(p';p) z_\beta(p'';p) \tag{38}$$

of the following integral operator

$$\langle u^{(s)}_{\alpha_1} \ldots \alpha_s \rangle \equiv \frac{l_m}{p} \int_0^p \mathrm{d}p' \int_0^{p'} \mathrm{d}p'' \, u^{(s)}_{\alpha_1 \ldots \alpha_s} \exp\{-y \mid p' - p''\mid\} \tag{39}$$

On writing the matrix elements of $\tilde{X} + \boldsymbol{b}$ in the more convenient form

$$\tilde{X}_{\alpha\beta} + b_{\alpha\beta} = U_{\alpha\beta} + I^{(0)} \eta_\alpha \eta_\beta \tag{40}$$

where the following designations are used

$$U_{\alpha\beta} \equiv \Delta_{\alpha\beta} + b_{\alpha\beta} \quad \eta_\alpha \equiv \langle X_\alpha \rangle + \frac{I^{(1)}}{I^{(0)}}$$
$$\Delta_{\alpha\beta}(y) \equiv I^{(2)}_{\alpha\beta}(y) - \frac{I^{(1)}_\alpha(y)\, I^{(1)}_\beta(y)}{I^{(0)}(y)} \tag{41}$$

one can find the matrix determinant

$$D(q^2) = I^{(0)}(y)\, U(y) \tag{42}$$

which equals the product of the positive integral $I^{(0)}(y)$ and any cofactor $U(y)$ of the matrix $\boldsymbol{U}$ with elements in eq 41. Thus, the conditions (eq 34) of finding the nontrivial spinodal branch will assume, within the framework of the approximation of interest, the following form

$$U(y) = 0, \frac{\mathrm{d}U(y)}{\mathrm{d}y} = 0 \tag{43}$$

where y is related to the wave vector q by relation 35.

In the case of binary copolymerization when

$$z_1 = -z_2, \quad I^{(1)} \equiv I^{(1)}_1 = -I^{(1)}_2, \quad I^{(2)} \equiv I^{(2)}_{11} = I^{(2)}_{22} = -I^{(2)}_{12} \tag{44}$$

the expression for the dimensionless amplitude of scattering (eq 28) reads

$$\frac{1}{J(q)} \equiv \frac{\rho(a_1 - a_2)^2}{I(q)} = \frac{1}{\Delta(y)} - 2\chi \tag{45}$$

where the dependence of Δ on y is determined by the expression

$$\Delta(y) = I^{(2)}(y) - \frac{[I^{(1)}(y)]^2}{I^{(0)}(y)} \tag{46}$$

The function $U(y)$, from which the spinodal can be found, is for binary and ternary copolymerization, respectively, given by

$$U(y) = -\Delta_{12} - \frac{1}{2\chi_{12}} \quad (\Delta_{12} = -\Delta, \chi_{12} = \chi) \tag{47}$$

$$U(y) = (\Delta_{12}\Delta_{13} + \Delta_{12}\Delta_{23} + \Delta_{13}\Delta_{23}) - \frac{2}{\mathscr{P}}(\Delta_{12}\chi_{12} + \Delta_{13}\chi_{13} + \Delta_{23}\chi_{23}) - \frac{1}{\mathscr{P}} \tag{48}$$

where $\Delta_{\alpha\beta}$ have been defined above (eq 41), while the quadratic polynomial $\mathscr{P}$ equals

$$\mathscr{P} = \chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2 - 2(\chi_{12}\chi_{13} + \chi_{12}\chi_{23} + \chi_{13}\chi_{23}) \tag{49}$$

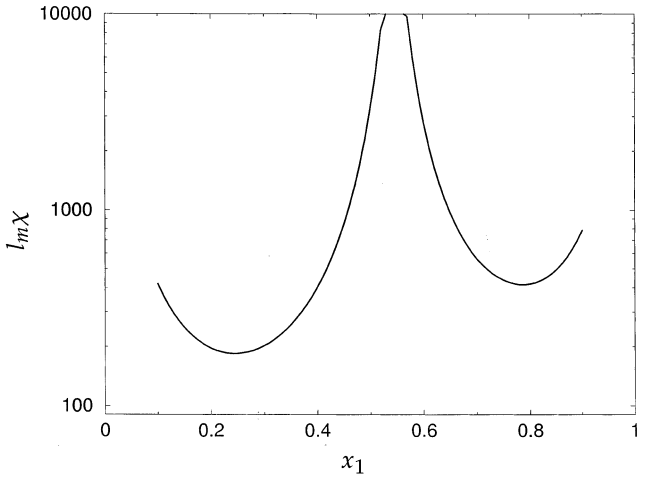

Figure 5. Spinodal $l_m\chi$ value as a function of the composition (x_1) for the products of anionic copolymerization of styrene and butadiene in toluene with sodium counterion ($r_1 = 0.42$, $r_2 = 0.30$)[26] (curve d in Figure 1).

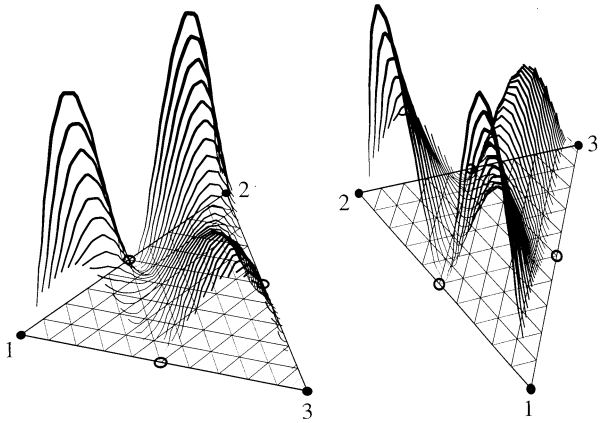

Figure 6. Qualitative behavior of the spinodal temperature as a function of the composition for a hypothetical ternary system with $r_{12} = r_{21} = 0.5$, $r_{13} = r_{31} = 0.1$, and $r_{23} = r_{32} = 0.05$. The χ-parameters scale as the inverse temperature $\chi_{\alpha\beta} = \epsilon_{\alpha\beta}/T$. The spinodal surface was calculated using $\epsilon_{12} = 330$ K, $\epsilon_{13} = 150$ K, and $\epsilon_{23} = 280$ K. The absolute value of the spinodal temperature depends on the average chain length.

Figure 5 shows the spinodal for the styrene/butadiene polymerization in toluene with a sodium counterion. The most striking feature is the divergence of $l_m\chi$ at the azeotropic composition ($x_1 = 0.55$), where a compositionally homogeneous copolymer is obtained. Finally, the application to a ternary system is exemplified in Figure 6, where the spinodal temperatures are presented for a hypothetical ternary system.

5. Semibatch Copolymerization

The copolymerization processes considered above were presumed to proceed in closed systems. Here the profile $P_\alpha(i)(\alpha = 1, ..., m)$ distributions of units along the macromolecules can be controlled by varying the solvent or the initiator. This results in a change in values of the constants $k_{\alpha\beta}$ of the chain propagation reactions. However, even at the same values of these kinetic parameters it is possible to obtain macromolecules with different profiles $\boldsymbol{P}(i)$, provided the synthesis is carried out under semibatch conditions. Within this operating regime monomers are added to the polymerization vessel during the synthesis, but nothing is removed from the vessel.

Let us take an m-component copolymerization in an ideal stirring reactor where a solution of monomers with their overall concentration M^{in} and molar fractions x_1^{in}, ..., x_m^{in} is added continuously with volume rate $q(t)$. Proceeding from the material balance of the reagents, the following kinetic equations for the monomer mixture composition in the reactor can be derived

$$\frac{dx_\alpha}{dt} = \frac{M^{in}}{M}\frac{d\omega}{dt}(x_\alpha^{in} - x_\alpha) + R^0 e^{-w}\frac{\Pi(\boldsymbol{x})}{w(\boldsymbol{x})}(x_\alpha - X_\alpha) \quad (\alpha = 1, ..., m) \quad (50)$$

Here the quantities $w(\boldsymbol{x})$ and $\Pi(\boldsymbol{x})$ have been introduced above (3) and (5), whereas the dependence of the function ω on time is given by the alteration of the rate with which the monomer mixture is fed into a vessel

$$\omega(t) = \ln\frac{V(t)}{V^0}, \quad \text{where } V(t) = V^0 + \int_0^t q(\tau)\,d\tau \quad (51)$$

To obtain a closed set of equations, eq 50 has to be complemented by an equation for the overall concentration of monomers M in the reactor

$$\frac{dM}{dt} = \frac{d\omega}{dt}(M^{in} - M) - MR^0 e^{-w}\frac{\Pi(\mathbf{x})}{w(\mathbf{x})} \quad (52)$$

In the absence of feeding by the monomer mixture ($q \equiv 0$, $\omega \equiv 0$) M is related to conversion p by the simple relationship $M = M^0(1 - p)$ so that the set of equations in (50) is reduced with allowance for eq 52 to eq 4 describing the copolymerization within a closed system. For a semiopen system the conversion is a rather ill-defined quantity, and instead, we will use the average chain length $\bar{l}$ as a means to denote the progress of the polymerization. For the following calculation it is convenient to introduce the variable

$$\vartheta \equiv \frac{\bar{l}}{l_m} = 1 - \frac{M^{in}}{M^0} + e^\omega\left(\frac{M^{in}}{M^0} - \frac{M}{M^0}\right) \quad (53)$$

coinciding with the conversion p in a batch polymerization processes. Note that ϑ unlike p may exceed unity. As $\bar{l}$ grows, the length distribution of the macromolecules becomes increasingly narrow so that for $\bar{l} \gg 1$ in a first-order approximation the polydispersity in length may be neglected. The molecules may be regarded as containing the same number of units $\bar{l}$.

The components of the vector of monomer mixture composition $\boldsymbol{x}$, obtained from the solution of eqs 50 and 52 being substituted into the expressions in (5), enable us to find the profile $P_\alpha(i) = X_\alpha(i/l_m)\eta_s(\bar{l} - i)$ (eq 17) of monomeric units of any type α of macromolecules formed in the course of "living" anionic semibatch copolymerization of an arbitrary number of monomers. For this process the following expression

$$\bar{\xi}_\alpha = \frac{1}{\bar{l}}\int_0^{\bar{l}} X_\alpha(i/l_m)\,di = \frac{1}{\vartheta}\int_0^\vartheta X_\alpha(\eta)\,d\eta = \frac{1}{\vartheta}\left[x_\alpha^0 - (1 - \vartheta)x_\alpha + (e^\omega - 1)\frac{M^{in}}{M^0}(x_\alpha^{in} - x_\alpha)\right] \quad (54)$$

may be considered as an analogue of formula 8. Relationship 54 allows the calculation of the average composition of the products of semibatch copolymerization $\bar{\zeta}$ at any stage. Once the solution of eqs 50 and 52 is

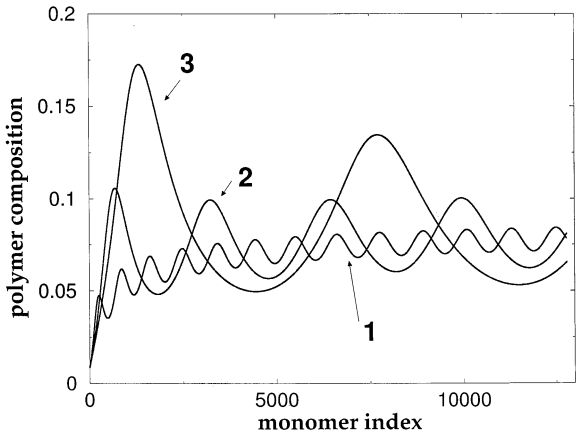

Figure 7. Composition of the copolymer vs the monomer index for a semibatch system of styrene/butadiene in toluene with lithium based initiator. A constant flow of 1.0 L/s with 1.0 mol/L monomers is applied to a tank with initial volume of 50.0 l containing initially 500.0 mol of monomers and 0.5 mol of initiator. Initial composition of the monomers is 10% of styrene. The feed has an oscillating composition $x_1 = 0.5 + 0.5 \sin(2\pi t/T)$ with period T of 600 (curve 1), 1200 (curve 2), and 2400 s (curve 3), which results in an oscillating composition profile along the chains (i.e., as a function of the monomer index).

found, it becomes possible to calculate the dependence on time of the concentrations of monomers $M_\alpha = Mx_\alpha$ and thus the elements (eq 15) of matrix **K**. Knowledge of this transition intensity between the states of the Markovian process of conventional movement along a macromolecule with labeled units and the recourse to the formulas reported in the preceding sections enable one to calculate chemical correlators, the amplitude of scattering and the spinodal of the melt of copolymers of interest. As an example, Figure 7 presents copolymer composition profiles obtained for the semibatch system of styrene/butadiene in toluene with lithium based initiator. A constant flow of 1.0 L/s with 1.0 mol/L monomers is applied to a tank with initial volume of 50.0 L, containing 500.0 mol of monomers and 0.5 mol of initiator molecules. The initial composition corresponds to 10% styrene ($x_1 = 0.1$). Feeds with different oscillating compositions are considered.

6. Conclusion

A theoretical discussion of the intramolecular inhomogeneities of macromolecules formed by "living" anionic copolymerization has been presented. If the inhomogeneity is pronounced the reaction results in the formation of tapered block copolymers capable, under certain conditions, of undergoing microphase separation with the formation of spatially periodic structures. Their periods, amplitudes, and morphology are controlled by the form of the copolymer composition profile and can be predicted theoretically. In the present paper, we restricted ourselves to the calculation of spinodals; however, the extension to more complete phase diagrams is, although tedious, relatively straightforward. This correlation between reaction conditions and phase behavior is essential for the choice of optimal conditions for the synthesis of advanced polymer materials for nanotechnology. The theoretical approach put forward in this paper provides the means to calculate the statistical characteristics of gradient copolymers prepared by anionic mechanism under batch as well as semibatch conditions, a necessary prerequisite for predicting their service properties.

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